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Solar assisted photo degradation of wastewater by compound parabolic collectors: Review of design and operational parameters

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A B S T R A C T

The use of solar radiation in wastewater treatment is a shift of artificial ultraviolet light to renewable and sustainable solar source. Various types of concentrating and non-concentrating solar reactors have been used in wastewater treatment applications. This study reviews the application, design and operational parameters of compound parabolic collector (CPC) for wastewater treatment. It is the most promising type of non-concentrating collectors which is better than concentrating collector. Details of CPC design parameters like reflective surface, absorbing tube material, absorbing tube diameter, and acceptance angle have been elaborated. Core operational parameters like photo catalyst types and their optimum concentration, pH and light intensity have also been undertaken. Application of CPC in wastewater treatment and water disinfection has been explained in the final part of the paper.

Contents

1. Introduction

The elimination of toxic chemicals from wastewater is presently one of the most important subjects in pollution control [1]. These pollutants may originate from industrial applications (petroleum refining, textile processing, etc.) or from household and personal care areas (pesticides and fertilizers, detergents, etc.); several of them are resistant to conventional chemical and biological treatment methods, such as coagulation, activated carbon adsorption, etc. As a result, the use of alternative treatment technologies that aim to transform them into their biodegraded form is a matter of great concern. The search for effective means of removing these compounds is of interest to regulate authorities everywhere [2].

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Advanced oxidation processes (AOPs) are very promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants. The main mechanism of AOPs is the generation of highly reactive free radicals like hydroxyl radicals ($OH^{\bullet}$) which are effective in destroying organic chemicals because of their high reactive electrophilic behaviour. The use of AOPs such as ultraviolet (UV)/hydrogen peroxide (H_2O_2), UV/H_2O_2/Iron (Fe^{2+}), UV/titanium dioxide (TiO_2) and UV/zinc oxide (ZnO) for wastewater treatment have been studied extensively. While potentially effective, most of the UV based AOPs have drawbacks in terms of high operational cost, which is mainly a result of high energy consumption. This drawback can be overcome by applying solar irradiation (sunlight) instead of artificial UV irradiation (UV lamps) [3].

The use of solar irradiation for the photo catalytic oxidation of organic contaminants in wastewater is a fast developing application [4]. The combination of solar light and catalysts has proven to be a promising alternative [5]. The energy needed to activate the semiconductor catalyst recommended for the solar detoxification process corresponds to UV component of the solar radiation. Selection of catalyst must be in such a way that it uses maximum fraction of solar energy [6]. In some cases, such as, removal of colour and reduction of chemical oxygen demand (COD) in industrial wastewater, photo catalytic oxidation may be the only effective treatment available [7]. There are two types of solar reactor designs generally used for photo catalytic degradation: concentrating and non-concentrating solar reactors. Non-concentrating solar reactors make use of both direct and diffuse components of solar ultraviolet radiation and have the potential for low cost development and greater efficiency [8]. In terms of wastewater treatment designs based on non-concentrating category are more mature having flexible working conditions, controlled concentration ratio (ratio of collector aperture area to the absorber area) and temperature. Compound parabolic collector (CPC) is the widely applied and best tested design with excellent efficiency in non-concentrating solar reactors. The aim of this study is to review the important issues regarding its design and performance in wastewater treatment applications.

2. Types of solar reactors

There are mainly two types of solar reactors named as concentrating and non-concentrating solar reactors for wastewater treatment [9]. Non-concentrating solar reactors are more effective in wastewater treatment as compared to concentrating solar reactors. Concentrating solar reactors are more efficient in energy generation because of their high solar radiations absorption capacity.

2.1. Concentrating solar reactor

The first photo reactors for solar photo catalytic applications designed at the end of the eighties were based on concentrating solar reactors [1]. Parabolic-trough collectors (PTCs) are most promising type of concentrating solar reactors which is proved to be effective for wastewater treatment. PTCs consist of a structure that supports a reflective concentrating parabolic surface. This structure has one or two motors controlled by a solar tracking system on one or two axes, that keeps the collector aperture plane always perpendicular to the solar rays (Fig. 1). In this situation, all solar radiation available on the aperture plane is reflected and concentrated on the absorber tube that is located in the geometric focus of the parabola. The size and length of the collector is small, which can translate into a reactor that is able to support higher pressures and a large amount of energy per unit volume [3].

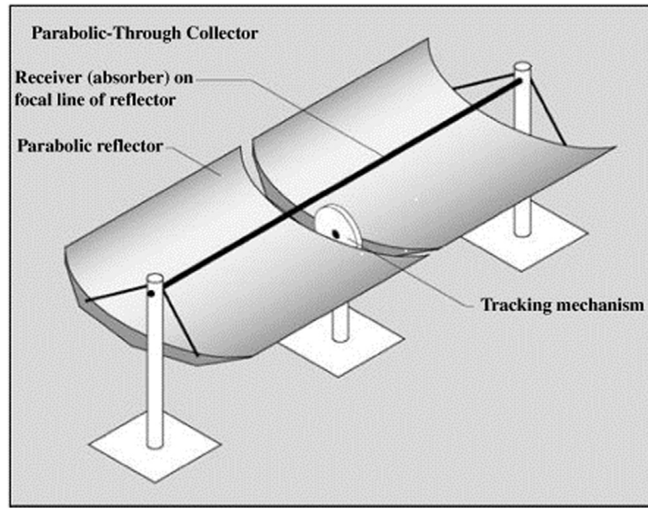


Fig. 1. Schematic figure of PTC [10].

PTC technology was relatively mature and existing hardware could be easily modified for the photochemical processes. The first outdoors engineering-scale reactor developed (in USA) was a converted solar thermal parabolic-trough collector in which the absorber/glazing-tube combination had been replaced by a simple pyrex glass tube through which contaminated water could flow. The first engineering-scale solar photochemical facility for wastewater treatment in Europe was developed by Plataforma Solar de Almerıa (PSA) research centre in Spain [4] using 12 two-axis, each consisting of a turret and a platform supports four parallel PTCs, with an absorber at the focus of each collector. Parabolic-trough collectors make efficient use of direct solar radiation and as an additional advantage; the thermal energy collected from the concentrated radiation could simultaneously be used for other applications. The reactor is small, while receiving a large amount of energy per unit volume. The flow is turbulent and volatile compounds do not evaporate, so that handling and control of the liquid to be treated is simple and cheap [11].

2.2. Non-concentrating solar reactor

Non-concentrating solar collectors are static systems with no solar tracking mechanism. They usually consist of parabolic or flat plate like technology, static devices oriented toward the equator at a specific inclination, depending on the latitude of the site. Their main advantage is their simplicity and lower manufacturing cost [12]. Non-concentrating collectors are cheaper than concentrating reactors because they have no moving parts or solar tracking devices. They do not concentrate radiation, so their efficiency is not reduced by factors associated with concentration and solar tracking.

Their support structures are easier and cheaper to install and less surface is required for their installation. Being static they do not project shadows on the absorber and reflector surface [11]. However, they may collect beam sunlight less efficiently on an energy basis, given that they present a fixed orientation to the incoming radiation. But they are much more adapted to small scale situations, and as stated above, they collect diffuse radiation. Because of great effort invested in small non-concentrating collector designs for other applications, a large number of non-concentrating solar reactors for solar photo catalytic process have been developed and tested all over the world [13] and particularly at PSA research centre in Spain [14]. An extensive effort in the design of small non-tracking collectors has resulted in the testing of several different non-concentrating solar reactors:

(a) *Free-falling film collector*: the process fluid falls slowly over a tilted plate or inside tubes with a catalyst attached to the surface, which faces the sun and is open to the atmosphere [15].
(b) *Pressurized flat plate collector*: consists of two plates between which the fluid circulates using a separating wall [11].
(c) *Solar ponds*: small, shallow on-site pond reactors [16].
(d) *Tubular collector*: consisting of many small tubes connected in parallel to make the flow circulate faster than a flat plate.
(e) *Trickle down flat plate collector*: based on a tilted plate facing the sun over which the process fluid falls slowly; a catalyst is normally fixed on plate surface.

Design of a robust system is not trivial, since they must be weather resistant, chemically inert and UV-transmissive [17]. In addition, flow is usually laminar, which presents mass transfer problems and vaporization of reactants. Use of tubular photo reactors has a decisive advantage of inherent structural efficiency of tubes, which are also available in a large variety of materials and sizes and a natural choice for a pressurized fluid system [13]. These systems require a significantly larger photo reactor surface and must be designed to support high operating pressures in order to pump fluid [18]. Under non-concentrating category different types of solar reactors are being used in wastewater applications like compound parabolic collectors, flat plate collectors, optical fibre collectors, well bell reactors, evacuated tube collectors, double skin sheet reactors etc.

Comparative analysis of concentrating solar reactor and non-concentrating solar reactor is being given in Table 1.

2.2.1. Compound parabolic collector (CPC)

Compound parabolic collectors come under the category of non-concentrating solar reactor and considered to be the most efficient and mature design in photochemical application. CPC reactors have given opportunity to use the best optics for low concentration systems and can be designed with concentration ratio close to one, thus it has both features of concentrating and one non-concentrating collectors [19]. CPC is made of two halves of parabola with closely located focal points and their axes inclined to each other. Incident rays within the angle between the two axes (acceptance angle of the CPC) are reflected with single or multiple reflections towards the region between the two focal points and get concentrated in that region. Thus, CPCs can accept incoming radiation over a relatively wide range of angles. By using multiple internal reflections, any radiation that is entering the aperture, within the collector acceptance angle, finds its way to the absorber surface located at the bottom of the collector [20]. Schematic diagram of CPC is given in Fig. 2.

On the basis of geometric configuration of absorber tubes, CPCs have been divided into four types: tabular, flat, fin and inverted vee. Fin or tabular absorber is illuminated on all sides, thereby requiring only half as much absorber material. This result in lower material costs, smaller conductive losses to the back, and gains in performance since the transient response is improved [21]. While in case of flat receiver configuration has a higher optical transmission due to its shape factor [22]. The benefit of CPC is intrinsic simplicity; cost effectiveness, easy to use and low capital investment. Reflector designs for CPC have ability to collect all direct and diffused UV radiation [23], resulting in more efficient UV based wastewater treatment. The design of conventional CPC has two disadvantages: (i) its height increases rapidly with aperture, making the structure unwieldy to handle and (ii) a sizable percentage of radiation incident within the acceptance angle suffers multiple reflections before reaching the receiver, resulting into a drop in its optical efficiency. These limitations can be captured by placing the focal points close to aperture. Reflected light on the back of absorber tubes is efficiently used by the pollutants inside the tubes to proceed photochemical reaction. CPCs have been widely studied at pilot plant scale but there are not many evidences regading commercial scale level. Factors inhibiting its performance at commercial level are slow overall rates, low quantum yields, low-order dependence of rates on light intensity, poisoning and fouling of the catalyst, and scavenging of active oxidizing agents by spectator species. Also, solar energy experiences diurnal and annual cycles and varies with weather patterns. The water being treated can contain chemicals that block the critical wavelengths necessary for photo activity and may require pre or post treatment [24].

Due to its tabular absorber tubes, high concentration ratio and controlled temperature range CPC is superior to other types of non-concentrating solar collectors. It has higher light captivity

Table 1
Advantages and disadvantages of concentrating and non-concentrating solar reactors.

Type of reactor	Advantages	Disadvantages
Non-concentrating solar reactor	No heating	Laminar flow
	Low cost	Vaporization of fluid
	High capital efficiency	Reactants contaminations
	High quantum efficiency	Weather resistance
	Turbulent flow	Only direct radiations
Concentrating solar reactor	No vaporization of fluid	High cost
	More practical use of supported catalysts	Low capital efficiency
	Small reactor tube area	Low quantum efficiency
	Availability of direct and diffuse radiations	Water overheating

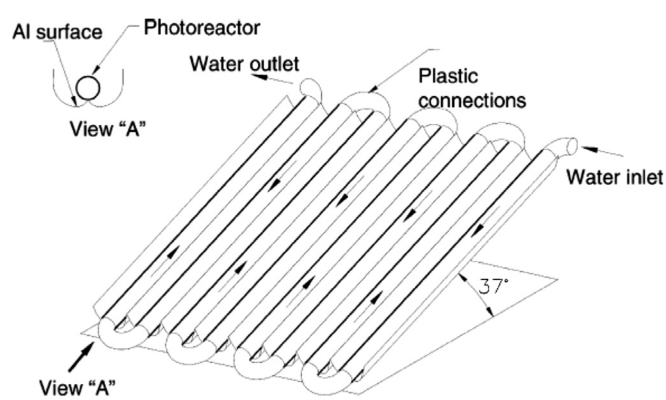


Fig. 2. Schematic diagram of CPC [3].

Table 2
Different types of non-concentrating collectors.

Reactor type	Name of reactor	Absorber type	Concentration ratio	Temperature range (°C)
Non-concentrating collector	(i). Compound parabolic collector (CPC)	Tabular	1–5	60–240
	(ii) Evacuated tube collector (ETC)	Flat	1	50–200
	(iii) Flat plate collector (FPC)			30–80

efficiency with smaller area under one sun operation [25]. Comparison of different types of non-concentrating collectors is given in Table 2.

All these factors contribute to excellent CPC collector performance in solar photochemical and photo catalytic applications. Detail of CPC design parameters is discussed below.

2.2.1.1. Reflective surface. For photo catalytic applications reflection of the wavelength between 300 nm and 400 nm is of special interest. The requirements for the optical quality of reflective surfaces in solar applications are usually related to the solar concentration. For CPCs, material ability to reflect UV light is more important as compared to high temperature achievement. As a reflecting material, aluminium is the best option owing to its low cost and high reflectivity. Mirrors based on aluminium are clearly the best option since this metal is the only one that is highly reflective in the ultraviolet spectrum of solar radiation (300–400 nm) [26]. This reflectance, furthermore, is very stable in this range. The ideal conditions of a reflective surface for applications of solar photocatalysis are the following [27]: (a) highly reflective in the UV range, (b) weather resistant, and (c) reasonable cost. The most critical conditions are clearly the last two.

Surfaces currently available which solve the problems and best comply with the requirements indicated above are: highly transmissive, weather resistant aluminised plastic film, anodised and electro polished aluminium surfaces. Aluminised plastic film based surfaces are prepared by attaching aluminised plastic on the surface to be used as the UV reflective element. The outside of this film had to be made of a very weather resistant plastic material with high UV transmittance on which a thin coating of metallic aluminium is vacuum deposited. Examples of this type of materials are ECP-244 (acrylic solar energy reflecting film), consisting of an 10 mm thick aluminium layer coated by a 76 mm acrylic surface (63% reflectivity between 280 nm and 385 nm) and SA-85P (metalized polymers used as reflecting material) consists of a 50 mm thick polyester packing, a 10 μm aluminium layer and a very thin 2.5 μm acrylic covering which makes its reflectivity higher (around 87%) [28]. The main advantage of this type of surface is its weather resistance ability as compare to metals [29]. The main problem is its lack of rigidity and needs to be attached on rigid substrate which not only increase cost but also affect reflectivity.

Considering these issues anodised and electro polished aluminium surfaces are considered to be more feasible. The anodised process consists of creating a thin layer of aluminium oxide (Al_2O_3) on the electrolitically deposited aluminium. Usually, thin layers of oxide (2–3 μm) are used to make to the metal surfaces somewhat resistant to abrasion. However, this technique is insufficiently protected for outdoor use, since the humidity or pollutants make the oxide coating continue to grow drastically, diminishing the UV reflectivity [26]. Thicker layers of oxide (up to 50 μm) are generally employed when anodised aluminium is used in engineering applications. Another interesting alternative is coating the aluminium with protective acrylic enamel, although there must always be a compromise between UV reflectivity and weather resistance. Recent developments in anodised aluminium films (both electro polished anodized [30] and organic plastic films [31]) represent a most acceptable raw material for the construction of highly efficient and weather resistant UV reflective surfaces which have been tested at Plataforma Solar de Almeria (PSA). Recent days chrome is also an attractive choice for reflective surface material for sunlight. It has been proved to be more efficient in performance as compared to aluminium but it is more expensive.

2.2.1.2. Absorbing tube material. The photochemical reactor must contain the working fluid, including the catalyst or the sensitizer, and must transmit solar UV light efficiently with minimal pressure-drop across the system. It must also provide good mass transfer from the fluid stream to an illuminated photo catalyst or a sensitizer surface. An adequate flow distribution inside the reactor must be assured, since a non-uniform distribution leads to a non-uniform residence time inside the reactor and as a result decrease in performance compared to that of an ideal flow. The choice of materials which are transparent to UV light and resistant to its destructive effects is limited. Temperature inside solar photochemical reactor can easily reach to 40–50 °C which is acceptable but for summer season when it reaches to 70–80 °C reactor must withstand this situation. Furthermore, reactor material must be inert to chemicals and resistant to high or low pH. Quartz has excellent UV transmission and resistance to temperature and chemicals, but it is costly for commercial applications. Fluoropolymers are also good choice because of their good UV transmittance and chemical inertness [32]. One of their greatest disadvantages is the wall thickness of a fluoropolymer tube which have to be increased to achieve a desired minimum pressure rating and lower UV transmittance. Borosilicate glass is a natural alternative for photo reactors. Low iron content borosilicate glass has good transmissive properties in the solar range with a wavelength of 285 nm [30].

Absorption of solar radiations below 400 nm cause oxidation of Fe^{2+} ions into Fe^{3+} which absorbs UV rays and as a result efficiency of solar degradation decreases [29]. The enhancement of transmissivity in the 300–400 nm region can only be attained by a strong reduction in iron content down to 50 mg kg^{-1} [33] Tripanagnostopoulos fabricated an asymmetric CPC collector with two separate absorbers in order to absorb and trap maximum solar radiation. At the same time they made the system cost effective and under controlled temperature range compared to flat plate collector using low cost material, but with lower concentration [34]. Azhari and Khonkar tried to improve the efficiency of the CPC system using modified absorber. They modified absorber by introducing two cavities in the appropriate location for radiation trapping [35].

2.2.1.3. Diameter of absorbing tube. In the designing process of CPC, diameter is an important factor. Flow pattern, travelling path length, absorbed light and active operation of catalyst are directly related with this issue. Uniform flow inside the reactor must be maintained all the time because non-uniform flow can cause non-uniform residence time condition which can be the cause of lowering the efficiency of the system ideal [36]. In heterogeneous wastewater treatment application like with the use of TiO_2 catalyst in suspension, sedimentation and deposition hydraulic circuit condition must be avoided so that turbulent flow in the reactor must be carried out [37]. In turbulent flow patterns, pressure loss is an important factor in limiting the design especially at industrial scale level where long reactor tubes are being used. For all these above stated reasons and also practical considerations absorber tube diameter should not be less than 20–25 mm and also photo reactor design should ensure the usage of all incoming photons [38]. In case of a catalyst introduction, wavelength range for photons absorption and strong scattering effects due to catalyst particles are very important issues. These factors must be considered in determining the optimum catalyst loading as a function of light-path length (diameter) in the photo reactor. Wavelengths where the catalyst does not absorb light are better for determining the optimum catalyst concentration as a function of light-path length. Under these conditions, measurement of photon losses is only affected by turbidity and it is easier to evaluate the effect of the photo reactor diameter. In Fig. 3 results of an experiment are being shown which shows that lower the diameter or path length more the light transmittance and less usage of catalyst and vice versa [39].

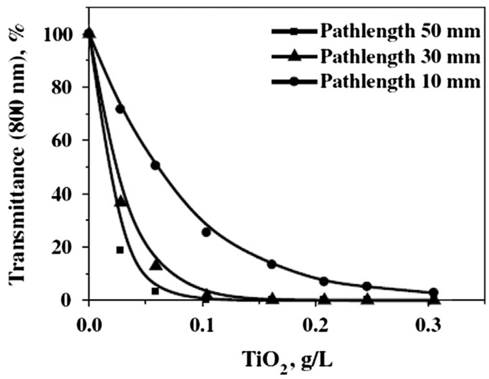


Fig. 3. Effect of absorbing tube diameter on transmittance in case of titanium dioxide [39].

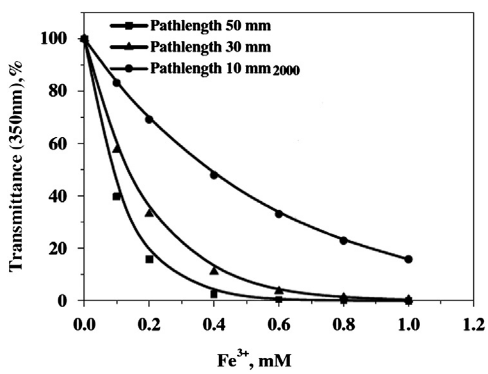


Fig. 4. Effect of absorbing tube diameter on transmittance in case of iron [41].

As these types of calculations are strongly affected by the experimental equipment because use of an electronic spectrophotometer is not the same with a lamp and quartz as with solar reactor. After many experiments with different solar reactors the optimum TiO_2 concentration obtained with sunlight is 200 mg/L [40] and diameters above 50–60 mm are not considered practical. The ideal diameter of the solar reactor must be in the range of 25–50 mm. Gernjak et al. [41] showed that iron concentration is affected more by light-path length than the TiO_2 process, but it also clarifies that the optimum diameter of the solar reactor is very similar in both cases. Formation of different complexes by iron can affect the above mentioned values as shown in Fig. 4.

2.2.1.4. Acceptance angle. Angle of acceptance is the angle with which CPC concentrate or collect radiation arriving at the surface of the reactor. CPC concentration ratio can be calculated by acceptance angle as given

$$CR = 1/\text{Sin}\theta_c$$

here *CR* is the concentration ratio which is used to describe concentrated amount of light energy achieved by a given collector and θ_c is acceptance angle for CPC. Acceptance angle is being elaborated in Fig. 5.

In Fig. 5 cross section of CPC is being shown and θ_c is the acceptance angle which solar radiation is making with the axis of CPC.

The normal value for the semi-angle of acceptance (ha), for photocatalytic applications is between 60° and 90°. This wide range of acceptance allows the absorber to collect both direct and a large part of the diffuse light with the additional advantage of decreasing errors of both the reflective surface and receiver tube alignment. A special case is the one in which θ_a is 90, whereby $C_{CPC}=1$ (non-concentrating solar system) and each CPC curve is an ordinary involutes. In this case all the UV radiation that reaches

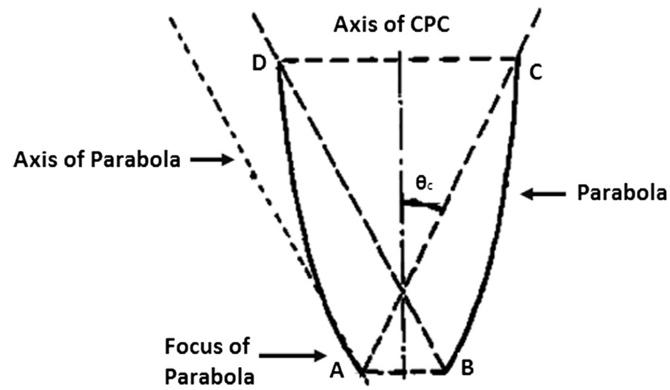


Fig. 5. Acceptance angle of CPC [42].

the aperture area of the CPC (not only direct) can be collected and redirected to the reactor. If the CPC is designed for an acceptance angle of +90 to −90, all incident solar diffuse radiation can be collected. The light reflected by the CPC is distributed all around the tubular receiver so that almost entire circumference of the receiver tube is illuminated and the light incident on the photo reactor is same that would be impinging on a flat plate. Accumulated energy and optical efficiency of CPCs are important considerations in photo degradation applications. These factors are strongly related with incident angle. Bandala studied the effect of incident angle on accumulated energy in oxalic acid degradation. Increasing angle above 60 reduces degradation while between 30 and 48 shows good results [43]. Optical efficiency shows the ability of a collector to accept radiations coming whole hemisphere above them. For all the collectors optical efficiency decreases when incident angle increases. In principle, the CPC has the best acceptance function from any direction, except for a small portion of radiation at very inclined angles, which is lost due to surface errors [44]. At Plataforma Solar de Almerıa Spain, different angle inclination have been tested and $\theta=37$ was considered to be the best. Later on same acceptance angle was tested and applied in different researches.

2.2.1.5. Radiation absorption. An important consideration regarding solar photochemical system is the requirement of an intermediate element to absorb the useful solar radiations. Radiations are normally absorbed and transferred to the photochemical process by catalyst or sensitizer. Depending on the phase of photo catalyst, photochemical process can be heterogeneous or homogenous. In heterogeneous system catalyst in solid phase is introduced with supported configurations. This would eliminate the need of recuperation but with the main severe objection of reduction in system efficiency. As the catalyst must be exposed to sunlight and in contact with reaction medium, support must be configured efficiently. It is important that reactants are present in illuminated zone and flow rate is not affected by pressure decrease. Heterogeneous assembly is efficient in perspective of high reaction rate, long life time and reasonable cost.

On the other hand homogeneous or slurry configuration have also advantages of low pressure decrease and excellent fluid to mass transfer. In this case catalyst is present in the same phase as target pollutant. Photo Fenton based applications where iron is used as catalyst is considered homogeneous in nature. In homogenous configuration there is no loss of absorbed light due scattering. If catalyst can be easily removed from the system, homogeneous configuration can reduce the size of solar reactor field and make it efficient and competitive as compare to heterogeneous systems. In absorption of the solar radiations diameter also plays important role because all the useful photons can be

kept inside the reactor and not to let go out without interception with target particles just by keeping the diameter relevance to system.

3. Working of CPCs

Role of absorbing tubes and reflecting material is very important in working with CPCs. Absorbing tubes are the major platform which will ensure the compatibility of solar irradiation for the pollutant degradation and excitation of photochemical reaction. Intensity of irradiation reaching at the absorbing tubes depends upon the reflecting material. The higher the reflective behaviour of material, the higher radiations prevail on the tubes and as a result efficiency of photochemical reaction increases. Other auxiliary parts are tank, mixer, circulating pump and temperature controller. Mixer not only ensures uniform composition of reagents but also plays important role in reaction efficiency and uniform mass transfer. Temperature controller keeps the reactor temperature under controlled conditions. In high temperature areas where temperature can have severe affect on reaction kinetics and raise water evaporation issues, controller provides a safe working environment. Flow rate which is adjusted by a simple flow metre, ensures appropriate residence time of fluid in tubes. In order to prevent suspended particles introduction to system a simple filtering media is used to prevent damage in pump and tubes [44].

Fluid is introduced in the tank and stirrer is started to mix and achieve uniformity. With the help of pump fluid is introduced in the tubes. Reflected radiations by reflector are absorbed by the tubes and photochemical reaction proceeds inside the tubes. In the presence of required conditions (oxidant, catalyst, pH etc.) solar irradiation generates high oxidizing species which attack on the target pollutant and degrade it into simple and easily removable compounds. Processed fluid leaves the tubes and goes back to tank by completing circle. Samples are collected at the end of tubes after specified time intervals. Working diagram of CPC is given in Fig. 6.

4. Operational parameters of the solar photocatalytic reactor

4.1. Types of photo catalysts

In photo degradation of wastewater pollutants catalyst addition is very important. Different types of catalysts have been introduced for

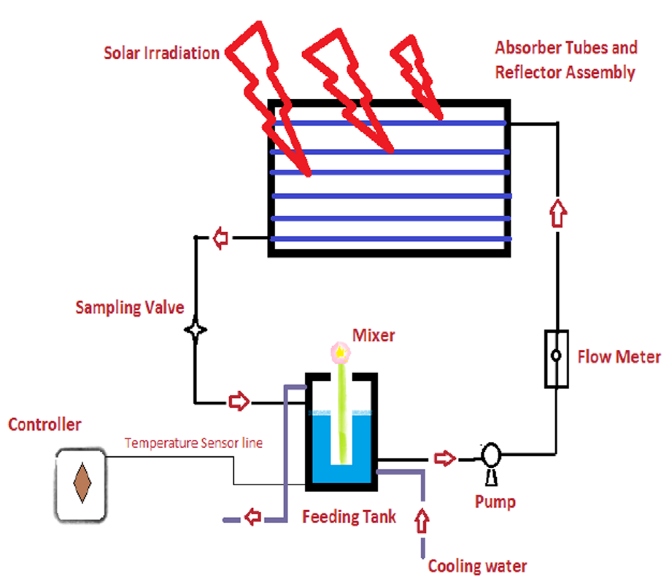


Fig. 6. Working of CPCs.

this purpose. Semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light induced redox processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band [45]. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron–hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl (oxidation potential 2.8 V) or superoxide radicals [46]. Above cited oxides and sulphides of semiconductors have band-gap energies (E_g) sufficient for promoting or catalyzing the photo degradation of pollutants present in wastewater. They include TiO_2 (E_g=3.2 eV), WO_3 (E_g=2.8 eV), $SrTiO_3$ (E_g=3.2 eV), Fe_2O_3 (E_g=3.1 eV for $O^{2-} \rightarrow Fe^{3+}$ transitions), ZnO (E_g=3.2 eV), and ZnS (E_g=3.6 eV) [47]. Among all these semiconductors, the most widely used semiconductor catalyst in photo induced processes is TiO_2 [48]. Although it has disadvantage of not being activated by visible light but it is advantageous over the others in that: (a) it is chemically and biologically inert, (b) photo catalytically stable, (c) relatively easy to produce, (d) efficiently catalyze reactions, (e) cheap and, (f) has no adverse effects on environment or humans [49].

The photo catalytic activity of TiO_2 depends on surface and structural properties of semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density. Particle size is of primary importance in heterogeneous catalysis, because it is directly related to the efficiency of a catalyst through the definition of its specific surface area. A number of commercially available catalysts have been tested for the photo catalytic degradation of various organic compounds in aqueous environment. Table 3 presents the specification and characteristics of some commercial TiO_2 samples.

When solar degradation rate of various pesticides and herbicides derivatives with various photocatalysts were compared, the efficiency of photocatalysts was shown to follow the order: P-25 > UV100 > PC500 > TTP [50]. The differences in the photocatalytic activity are likely to be related to the differences in the specific surface areas, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface. Iron oxide is another prominent catalyst applied in photo Fenton process. Solar photo-Fenton degradation of a mixture of five commercial pesticides was evaluated employing two iron species (Fe^{2+} and Fe^{3+}) separately at three iron concentrations (5, 20 and 55 mg/L) [51]. Modified solar photo Fenton reaction by using steel scrap as iron source offers greater possibilities for practical application of solar photo Fenton reagent as compared to traditional way out. It was observed that steel scrap acted as a heterogeneous catalyst for the activation of hydrogen peroxide. The modified solar photo Fenton process was found to be very efficient for decolourisation of real textile dyeing wastewater. The optimal concentration of H_2O_2 and steel scrap was 15 mL/L and 1 g/L, respectively at pH 3 [52].

Table 3
Types of commercial TiO_2 catalysts [55].

Type of TiO_2	Specific surface area (m^2/g)	Crystal size (nm)	Composition
P-25	50	21	75% Anatase, 25% rutile
PC 500	287	5–10	100% Anatase
UV 100	250	5	100% Anatase
TTP	9.82	N/A	N/A
PC 10	10	65–75	100% Anatase
PC 50	54	20–30	100% Anatase
Rhodia	150	N/A	100% Anatase

4.2. Catalyst loading

The amount of catalyst is one of the main parameters for the degradation studies. The catalyst loading affects both the number of active sites on photo catalysts and the penetration of solar light through the suspension consequently leading to enhanced production of •OH radicals. Although as the catalyst loading increases, the number of active sites increases but at the same time penetration of the solar light decreases due to shielding effect [53]. Furthermore, rate may decrease as a result of loss in surface area available for light-harvesting occasioned by agglomeration (particle–particle interactions) at high solid concentration [54]. In such a condition, a part of the photo catalyst surface probably becomes unavailable for photon absorption thus bringing little stimulation to the photo catalytic reaction. Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime [47]. Optimum amount of photo catalyst can be estimated using the optical data expressions reported by Li Puma [55,56]. In their study, the optical thickness is proposed as a key parameter to estimate the amount of catalyst for an optimal absorption of solar irradiation. However, besides the optimal thickness values, several important parameters as type of pollutant, reactor geometry, and the used radiation also affect the reaction rate [47]. Krutzler has indicated that type of wastewater, travelling path length in the reactor and flow rate are also important for the determination of optimum catalyst loading [57]. Using ZnO and solar light, the photocatalytic degradation rate of 4-Nitrophenol (4-NP) was observed to increase up to 0.6 g/L and then remain constant as the ZnO concentration increases to 0.8 g/L [58]. Using C-doped TiO_2, Xiao has demonstrated the effect of catalyst loading (0.5–4.0 g/L) on the solar photocatalytic degradation of methylene blue in the order $1.0 > 2.0 > 4 > 0.5$ g/L. They reported lower degradation at high catalyst loading with high turbidity due to C-doped TiO_2 nano particles [59].

4.3. pH effect

An important parameter in the heterogeneous photocatalysis is the reaction pH, since it influences the surface charge properties of the photocatalyst and adsorption behaviour of the pollutant and the size of aggregates formed [47]. pH effect depends on the nature of the pollutant being treated, catalyst type and the types of AOPs applied. Dye solutions [60] and paper mill wastewater treatment [61] has been efficiently done in alkaline pH conditions while phenol [62] has been degraded in acidic pH range. In the same way pH can affect the performance of photocatalyst. TiO_2 and iron oxide were used as catalysts in diclofenac degradation under acidic conditions. Changing iron oxide concentration under strong acidic conditions has shown no effect on decomposition of diclofenac due to iron precipitation and pollutant re-dissolution. On the other hand TiO_2 has shown excellent results under same pH because of no any precipitation. pH defines the surface charge of the photo catalyst [63]. For every catalyst there is a particular pH value called as point of zero charge (PZC) at which total surface charge density is zero. Charged catalyst particles are mobile, particle size remain constant and light extinction measurement show a constant concentration of particles in suspension while at PZC, lack of particles stability and aggregation happen [35]. Generally, the pH changes can have an ambiguous result not only on the mode of adsorption of the pollutant substrate on catalyst surface, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes in the surface [64]. Three possible reaction mechanisms can contribute to pollutant degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band. The importance of each one depends upon the substrate nature and pH [54]. Mostly it happens by the attack of hydroxyl radicals on pollutant. In an acidic medium, photo generated holes react with water molecules to produce hydroxyl radicals. On the other hand at alkaline pH, the negative surface of the TiO_2 with OH^- ions acts as an efficient trap for the photo generated holes and hydroxyl radicals are produced [65].

4.4. Light intensity

Light intensity is important factor in photocatalytic degradation which determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation of photocatalysis, electron-hole formation in the photochemical reaction is strongly dependent on the light intensity [66]. Under the higher intensity of light irradiation, the enhancement was considerably higher because of predominant electron-hole formation, and hence, electron–hole recombination is negligible. However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals as a result of decreasing the dye degradation efficiency [54]. In most cases the reaction rate exhibits low-order (often 1/2 order) dependence on light intensity, which means that photoefficiency decreases with increasing intensity. The dependence on light intensity is critical in the solar application of concentrating collectors or one-sun reactors. A concentrating system would allow the use of a smaller reactor in comparison to a one-sun system where the whole collector area is the reactor [67]. Several researchers have determined that the dependence of degradation rate on light flux is first order at low light intensities and half order at high light intensities [68]. The intensity at which the rate goes half order depends largely on the redox system that is being investigated. For the simple case of organic oxidation using dissolved O_2 as the oxidant, the dividing line is about an intensity of one sun in the 300–400 nm region, which is about 4×10^{-4} Einstein/s/m^2 [69]. Low-order dependence on light intensity is observed when the chemical steps are slow and cannot use electrons and holes as fast as they are generated. Consequently, adding photons too rapidly results in high concentrations of electrons and holes in the semiconductor and hence high recombination rates [68]. Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency [70]. Degradation rate constant and efficiency is strongly affected by the irradiated light intensity. Solar photocatalytic degradation efficiency of thiram increases up to 0.4 mW/cm^2 [71] and in case of bishphenol A (BPA) this trend is observed up to 0.35 mW/cm^2 [72].

5. Applications

5.1. Solar photo catalytic degradation of refractory organic compounds

Compound parabolic collectors have been extensively used for the destruction of variety of refractory organic compounds into harmless or least harmful products like CO_2, H_2O and simple minerals acids. In general, the types of polluting compounds that have been degraded include alkanes, halo alkanes, aliphatic alcohols, carboxylic acids, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides, and dyes [73]. Practical applications of solar photo catalytic degradation have been studied and developed most intensively for heterogeneous iron (Fe), TiO_2 and ZnO photo catalysis. There is no general rule; each case is different depending upon pollutant under study. Application of CPCs in photo catalytic degradation of various organic compounds has

been summarized in Table 4. Detail of operational parameters and process efficiency for each case is also given.

5.2. Solar photo catalytic disinfection of water

Natural sunlight as a killing agent for microorganisms was first described in 1877 [86]. Modern research in this field aimed to obtain pathogenic organisms free drinking water with lower cost. During recent years, work has concentrated on batch exposition to natural solar radiation, mainly small volumes (1–1.5 L) of untreated (or polluted) water in transparent vessels irradiated for periods of up to 8 h. This simple method, commonly known as Solar Water Disinfection (SODIS), has been proven successful for a wide variety of pathogens [87]. Although SODIS is very effective for household drinking water treatment, it is not feasible for larger volume. The resistance of microorganisms to solar radiation has been studied by several authors and found to vary from one type to another [88]. Often *Escherichia coli* (*E. coli*) are chosen as the reference enteric coliform bacterium in many studies. This bacterium is also widely recognized as an “easy” target for disinfection, since it is relatively simple to inactivate by solar radiation as shown in a number of related articles [89]. Use of photo catalyst like TiO_2 has shown improved results compared to simple solar disinfection [90]. For example disinfection of *E. coli* in the presence of TiO_2 catalyst has shown 99% inactivation in 90 min [91]. In another study, solar photo Fenton disinfection of natural organic compounds present in river water was observed in 24 h [92].

Lee et al. [93] and Lonnen et al. [87] demonstrated that the solar disinfection batch-process is unfeasible for the inactivation of cysts of the waterborne protozoan like *Acanthamoeba*, *Polyphaga* and for *Bacilus subtilis* spores. Nevertheless, the study also showed that fungal pathogens such as *Candia albicans* and *Fusariun solani* are readily inactivated using the solar disinfection technology. Kehoe et al. [94] proved that Type I *Shigella dysenteriae* is very sensitive to solar disinfection batch processing and is easily inactivated even under overcast conditions. Mendez et al. [95] investigated the feasibility of using batch-process solar disinfection for *C. parvum* oocysts in water. Proper evaluation of the solar radiation standardization parameters used for photocatalytic treatments is obviously a critical matter. In this sense, Rincon and Pulgarin have made a fundamental contribution to establish a method of assessing the bactericidal inactivation rate in solar photocatalytic processes for drinking water [96]. They found solar UV dose for disinfection is not sufficient as a system efficiency indicator. They have proposed a new parameter, “effective disinfection time (EDT)”. EDT is defined as the treatment time necessary to avoid bacterial re-growth after 24 h (or 48 h) in the dark after photo treatment. In both, natural and deionised water, *E. coli* cell inactivation was more effective in the presence of TiO_2 than to the just solar light irradiation. The presence of Fe^{3+} also accelerates *E. coli* inactivation under simulated sunlight [97].

6. Conclusion

This review deals with the design of the compound parabolic collector (CPC) and its (i) industrial wastewater treatment and (ii) water disinfection applications via sunlight induced advanced oxidation processes (AOPs). While potentially effective, most of the UV light induced AOPs have drawbacks in terms of high operational costs, which is mainly a result of high energy consumption. The use of sunlight enables to move towards natural and unlimited source of UV light which is a key agent in photo based AOPs. Solar reactors replace the artificial UV resources and provide inexpensive, renewable, and sustainable solution for wastewater treatment and water disinfection.

This paper has reviewed the designing of compound parabolic collector (CPC) and its application in photo catalytic wastewater treatment. CPC is the most mature reactor type of non-concentrating solar reactors that show better performance compared to concentrating solar reactors. Reflective surface and absorbing tubes has key role in operation, therefore material selection and construction of these components needs special attention. This acceptance angle and radiation absorption phenomenon is important parameters for design. CPCs work in continuous flow system and during operation mixing, flow rate and temperature of the system can be controlled easily. Catalyst type, its optimum amount, pH of the system and light intensity

Table 4
Application of CPCs in wastewater treatment.

Pollutant types	Pollutant Conc.	Catalyst type	Catalyst conc.	pH	Oxidant type and conc.	Efficiency	Time	Ref.
AMBI	1 mM	Fe^{+3}	0.1 mM	N/A	10 mM H_2O_2	90% COD removal	N/A	[74]
Remazol brilliant blue R-A	N/A	Fe^{+3}	0.5 mM	N/A	2281 mg/L of H_2O_2	100%colour removal and 85% TOC removal	8 h	[75]
Azo-dye acid orange 24	N/A	Fe^{+2}	0.1 mM	N/A	5 mM of H_2O_2	85% colour removal	65 min	[76]
4-Chloro-2-methylphenoxyacetic acid (MCPA)	186 mg/L	Fe^{+2}	1.0 mM	3	N/A	75% TOC reduction	2 h	[77]
Reactive blue 4	20 ppm	Fe^{+2}	7 ppm	2.5	120 ppm of H_2O_2	Complete removal of colour and COD	1 h	[78]
Mixture of commercial pesticides	200 mg/L	Fe^{+2}	20 mg/L	2.8	16 mM H_2O_2	75% TOC reduction	4 h	[79]
Phenol	180–733 mg/L	Fe^{3+}	20 mg/L	7	H_2O_2, H_2O_2/phenol = 5.5	100% Degradation 85% COD reduction	1 h	[62]
Phenolic compounds	20 mg/L	Fe^{+2}	20 mg/L	4	H_2O_2, 40 mg/L	Total elimination of original pollutants and 94% TOC	5 h	[80]
Dihydroxy-benzene compounds	34 mg/L	Fe^{3+}	1 g/L	5	H_2O_2, , 60 mg/L	Mineralization higher than 80%	6 h	[81]
Emerging contaminants in wastewater treatment plants	750 μg/ L	TiO_2	50 mg/L	4	N/A	75% Degradation	100 min	[82]
Pesticides	1000 μgL	Fe^{+2}	140 mg/L	2.8	18 mM of H_2O_2	79% Mineralization and total pesticide removal	N/A	[83]
Ibuprofen	20–200 mg/L	TiO_2	0.1–1 g/L	4.5	N/A	50% TOC reduction	2 Days	[57]
4-Chlorophenol	3 mM	Fe^{2+}	0.75 mM	2.8	H_2O_2, 45 mM	90% Degradation	30 min	[84]
Cyanide-containing water	60 ppm	Fe^{2+}	8 ppm	3.3	H_2O_2, 2000 ppm	100% Degradation 90% TOC reduction	N/A	[84]
Orange II aqueous solutions	5 ppm	Fe^{2+}	2 ppm	3.5	H_2O_2, 225 ppm	100% COD reduction, 80% TOC reduction	180 min	[85]

directly affect the photo catalytic degradation of pollutants. CPCs have been found excellent not only in photo catalytic degradation of refractory organic compounds but also in solar photo catalytic disinfection of water.

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